TEMPERATURE AND STRESS DEPENDENCE OF THE SHAPE MEMORY EFFECT PRODUCED BY ALLOYING ADDITIONS IN Cu-Al-Ni ALLOYS

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ABSTRACT.-The effect produced on microstructure and properties of CuAlNi alloys by additions of elements such as manganese and boron have been studied. Ductilities between 4-6% at room temperature and 12-16% at high temperature (250-300°C) have been achieved.These high strains were produced in all cases by the formation of stress-induced martensite variants which are favourable to produce maximum elongation at each temperature.

INTRODUCTION

The use of the shape memory effect at high temperature is based on the possibility of obtaining a martensitic/reverse transformation which produces enough accumulated strain to induce the shape change. This can be obtained by suitably training the specimen. One of the ways to achieve this is thermal cycling under constant load such as to stress-direct the austenite-to-martensite transformation. The degree of shape recovery will depend on the stress applied during this process and on the number of cycles producing the accumulated strain. The possibilities of training the material will depend on the strength and ductilities that it can sustain at the temperature at which the stress-induced shape change is to be used.
One type of alloy suitable for high temperature applications (150-200°C) is based on the $(CuNi)_3Al$ composition. This alloy has been shown to be rather brittle, due to the presence of the γ_2 phase (Cu_9Al_4) in some cases but sometimes intergranular failure has been observed without this phase being present (1,2). One possible way to improve ductility is the addition of suitable alloying elements. Elements like manganese can lower the electron/atom ratio (3) such that the formation of γ_2 phase can be suppresed while zirconium and boron can be added to refine the microstructure (4). The effects of these elements on ductility as well as on the transformation temperatures and on any modifications of the structures formed by high temperature deformation of the parent phase have been the aim of this study.

EXPERIMENTAL

The alloys used for this study had a basic composition Cu-12Al-4Ni-3Mn (wt%) with additions of different amounts of boron, namely 0.4% (M2), 0.1% (M4), 0.04% (M5) and 1% ZrB_2 (M6). They were prepared by induction melting under a helium atmosphere. The alloys were subsequently heated at 820°C for 30 minutes prior to extrusion at this temperature. Two treatments were carried out on the extruded bars:

an anneal at 820°C for 30 minutes followed by a water quench and sometimes an additional anneal of 30 minutes at 300°C and finally air cooled. All heat treatments were carried out under argon atmosphere.
Tensile tests were performed on the heat treated materials at room and between 150°C and 350°C . The tensile specimens used had a gauge length of 20 mm and were 3 mm in diameter. The specimen surfaces were electrochemically polished prior to testing using a solution of 40% orthophosphoric acid in water. All the tensile tests were carried out at a strain rate of $5x10^{-5}$ s^{-1}using a Schenck Universal testing machine equipped for high temperature experiments Microstructural studies from the as-cast, annealed and deformed materials were performed by optical and electron microscopy and by X-ray diffraction analysis.

RESULTS AND DISCUSSION

The measured grain sizes from the alloys obtained ranged between 100-140 μm in the material treated at 820°C followed by water quench to about 150-250 μm in the materials further annealed at 300°C and slowly cooled.These are very small grain sizes compared to conventional CuAlNi alloys reported in the literature (5). Therefore the addition of manganese and boron as alloying elements appears very efficient in terms if grain refinement and also in terms of their stability during heat treatments. The crystallographic structure corresponding to the martensite phase was analysed in all cases as the orthorhombic phase 18R of lattice parameters a=0.445 nm, b=0.529 nm and c=3.820 nm. There was no visible difference between the structures of the martensites obtained after the different heat treatments, only a different degree of long range order, characterised by the extent of splitting of some of the X-ray peaks (6), dependent on the boron content of the alloy (7); the alloys with higher boron content had a lower degree of order.
The parent phase obtained after the reverse transformation had taken place during the "in situ" heating experiments carried out in the TEM was the DO_3 structure.The characteristic transformation temperatures measured during these "in situ" experiments were A_s= 145°C, A_f= 190°C, M_s= 80°C and M_f=40°C. It was difficult to distinguish any differences in transformation temperatures between the alloys with different compositions since the kinetics of a thermoelastic transformation depend on the heating rate during the experiment and this was very difficult to control in the TEM.

Typical tensile curves obtained from the tests performed at different temperatures are illustrated in figure 1. We note that at room temperature the elastic slopes of the curves are very different depending on the treatment given to the alloys. The slope becomes negative for the specimens treated at 820°C followed by water quench while after giving a further treatment at 300°C followed by air cooling this does not occur (see fig. 1a). This appears to indicate that after the quench internal stresses are present in the martensite which are relieved by the applied stress producing an elastic strain of opposite sense. In figure 1b we compare the curves obtained from one of the alloys (M4) during tests at different temperatures. We see that a lower strain hardening rate is observed (plastic slope less steep) with increasing testing temperature. In figure 1c we illustrate the typical behaviour observed in all the alloys during high temperature deformation. In this figure we also show an example from a complete cycle obtained on unloading the specimen after a given strain, this was also similar in all cases. In the particular case shown, out of 5% total strain, 3.7% was recovered on unloading
Comparing these curves with those from previous studies made in polycrystalline CuNiAl alloys (2) we notice that at low testing temperatures ($T_d < A_f$) similar non-recoverable strain was obtained. However those alloys tested at higher temperatures ($T_d > A_f$) fractured before any plastic strain occurred and it was not possible to

determine whether a pseudoelastic behaviour (strain totally recovered) could be observed. It was assumed that if the brittle behaviour could be avoided, the same pseudoelasticity as that obtained from single crystals (8) should be seen. In the present study, non-recoverable strain is observed on unloading after tensile tests made at temperatures higher than A_f. As large plastic strains have been accomplished during these tests, it is concluded that the pseudoelastic behaviour will not be obtained in these ductile alloys. This behaviour can be understood from the observed microstructures after cooling the deformed specimens. The martensite variants formed by deformation at high temperature are so stable that they do not allow the formation of thermal martensite during cooling. This can be seen in Figure 2 where the head of the specimens (non-deformed) exposed to the same temperature during deformation shows the typical thermal martensite after cooling while the deformed gauge shows the stress-induced martensite formed during the tensile tests at 200 or 300°C. This behaviour was the same for all the alloys irrespective of the boron content. Also the number of stable stress-induced martensite variants decreased with the increase in deformation temperature as evidenced from figures 2b and 2c.

From the tensile curves obtained on the specimens that had been annealed for 30 minutes at 300°C after the water quench, the values of yield stress,$\sigma_{0.2}$, tensile strength, σ_{max} and ductility, ε, were obtained, Figure 3 shows the plots of yield stress (3a) tensile strengths (3b) and ductility (3c) as a function of testing temperature for all the alloys. To explain the decrease in yield stress observed between 20 and 150°C we need to discuss the mechanisms occurring at these temperatures. At a deformation temperature T_d= 20°C, the specimen has a fully thermally-induced martensitic

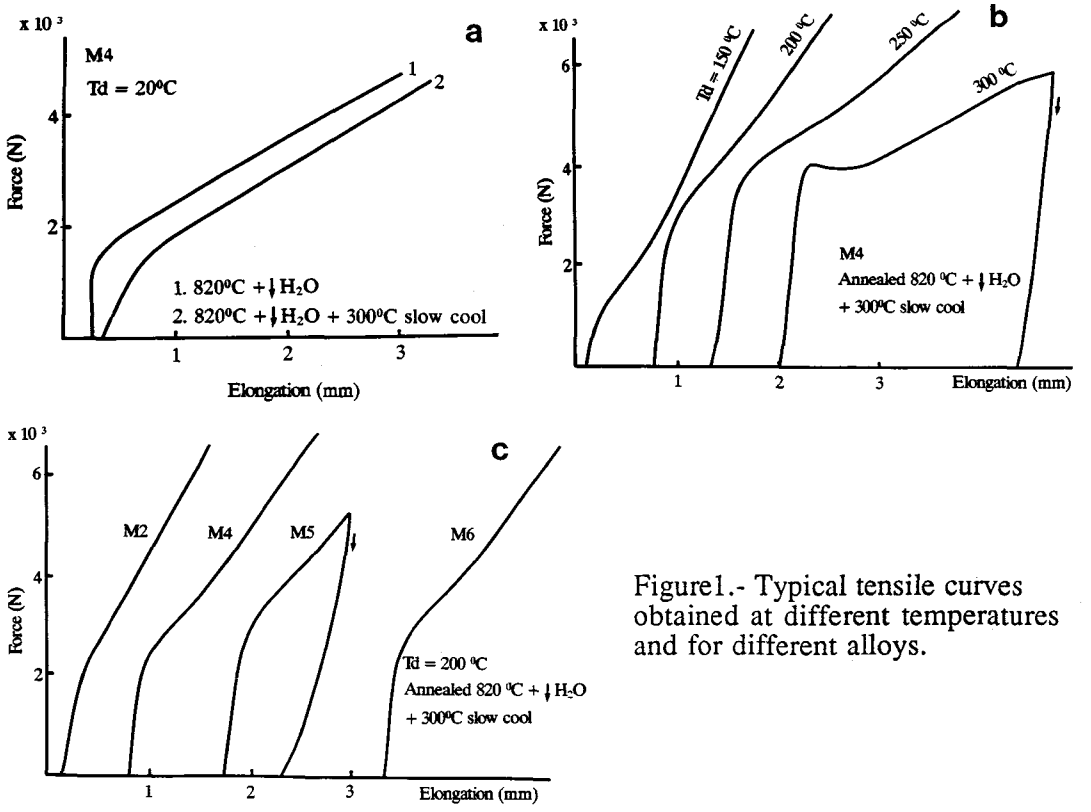


Figure1.- Typical tensile curves obtained at different temperatures and for different alloys.

structure ($T_d < M_f$) and the deformation will proceed by migration of twinning interfaces within the martensite phase and by the coalescence of certain variants. At 150°C we have $M_s < T_d < A_f$ and the deformation is only due to growth of induced martensite favoured by the presence of the stress. If the yield stress is lower at 150°C than at 20°C this means that growth of martensite variants favoured by the stress is easier (requires a lower stress) in the parent phase. This represents a lower energy being required to grow the most stable martensite variants in the parent phase than in competition with the other martensite variants. The increase in ductility and tensile strength (see figure 3) confirms the easier movement of these interfaces at 150°C producing less stress concentrations and therefore a more ductile mode of fracture than at room temperature.

The important increase in yield and tensile strengths observed at 200 and 250°C ($A_f < T_d$) represent the higher stress required to supplement the driving force necessary to produce the martensitic transformation as defined by the Clausius-Clapeyron equation (9). Also when strain-induced martensite is formed the ductility of the alloy increases substantially since the martensite variants that form preferentially are those that contribute to the maximum elongation of the specimen (this increase in ductility is illustrated in figure 3c). The slight decrease in strength observed at 300 and 350°C ($A_f << T_d$) occurs because the parent phase probably deforms before the stress-induced martensite appears. This is confirmed by the stress reduction observed in the tensile curve (see figure 1c) after about 1% strain which seems to correspond to the moment of strain-induced martensite formation.

From the results shown in Figure 3c we note that the average ductility for the tests performed at room temperature was 4-6%. The total amount of strain achieved increased continuously with increase in testing temperatures up to 300°C with a slight decrease being observed at 350°C for all the alloys. It is interesting to note that the highest ductilities were achieved for the alloys with 0.1% boron and 1% ZrB_2. SEM observations of the fracture surfaces have shown that the measured ductilities correspond well with the fracture modes seen in each case. Mixed modes of intergranular and transgranular failures were typically observed after deformation at the lower temperatures (namely 20-200°C) with more of the dimpled surface areas being observed for the higher temperatures. After deformation at 250 and 300°C the fracture mode appeared intergranular at low magnifications but detailed study of the grain boundary surface areas showed a very pronounced dimple structure indicating that a large amount of strain had occurred prior to the final decohesion of the boundaries. Figure 4 shows some examples of these ductile modes of fracture.

The strengths obtained from all the alloys where an anneal at 820°C followed by a water quench was given were very similar to those obtained after further annealing at 300°C and slowly cooled. However the former were even more ductile such that values of 15-16% deformation were reached when deforming at 300°C.

The ductilities and tensile strengths of the alloys containing 0.1% boron (M4) and 1% ZrB_2 (M6) present the highest values. On the other hand, the ductilities of the alloys containing the lowest (M5) and highest boron concentrations are almost equal even though the tensile strength of the latter is much higher. This is due to the higher strain hardening rate exhibited by the alloys containing more boron which probably depends on the effect that boride particles have on reducing stress concentrations and therefore on increasing the capacity of the material to accommodate strain.

Understanding the effect of temperature and stress on the ductility of these alloys, together with the observation of stabilised stress-induced martensite variants for each condition has made it possible to foresee the intrinsic shape memory properties that can be achieved by training these materials. Since the pseudoelastic effect is not present in the polycrystalline alloys, training will have to be carried out by thermal cycling at constant stress or strain . Since the yield stress at temperatures $T_d > A_f$ (200-250°C) is

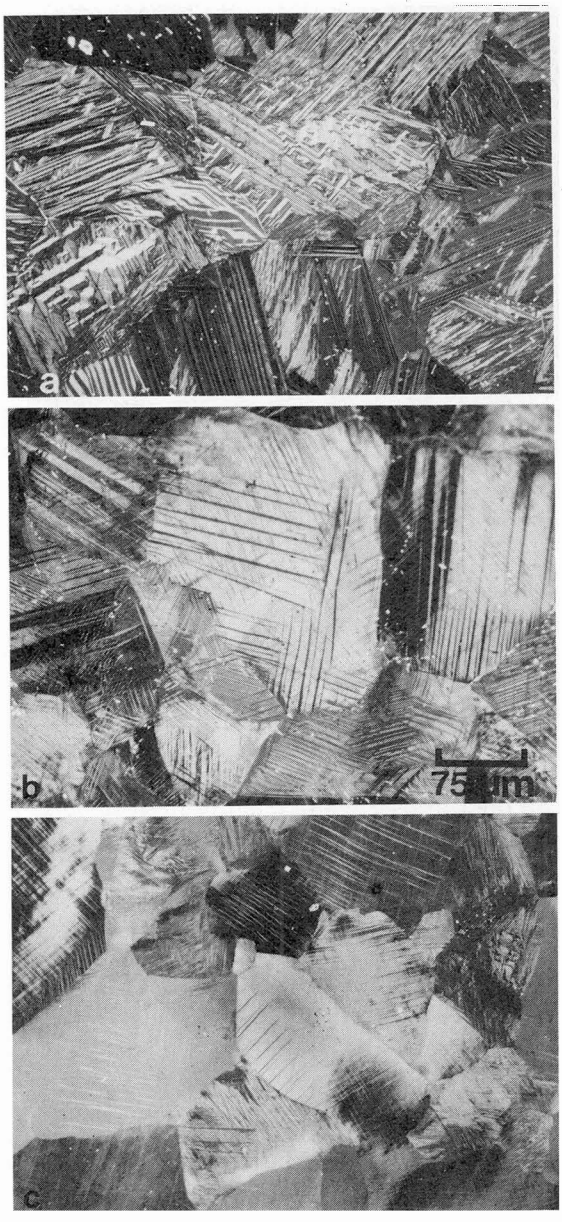


Figure 2.- Martensitic structures obtained after high temperature deformation, unloading and cooling : a) Non-deformed head of the specimen after deformation at 200°C, b) deformed gauge of the specimen after deformation at 200°C, c) deformed gauge of the specimen at 300°C.

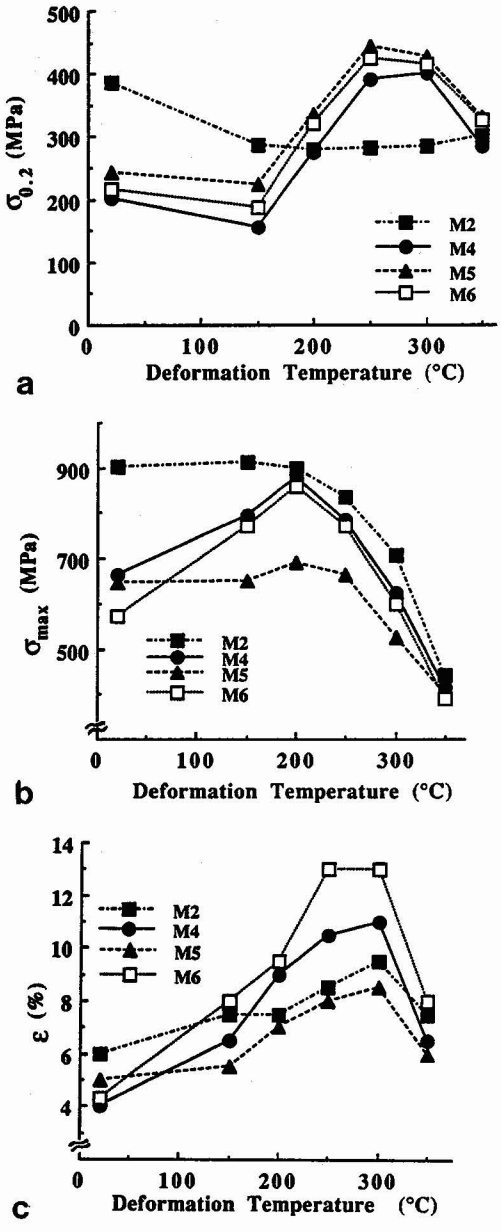
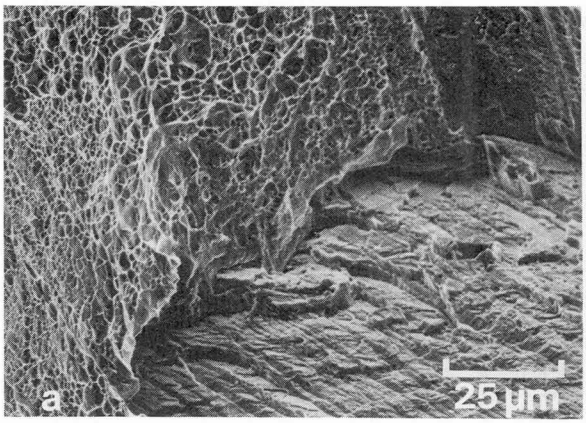


Figure 3.- Plots of a) yield stress, b) yield strength and c) ductility as a function testing temperature for all the alloys.



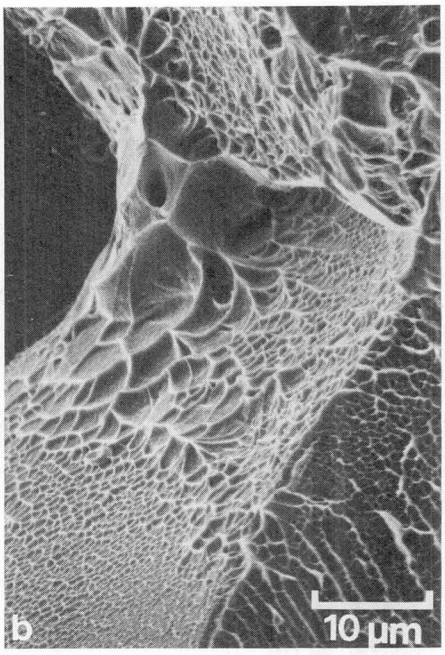


Figure 4.-Typical fracture surfaces observed from all the alloys: a) Deformation at T_d=20°C,b) The grain boundary surfaces show a dimpled structure after deformation at 300°C.

much higher than those at temperatures $T_d < A_s$ (20-150°C) for all the alloys except that rich in boron (M2) it will be possible to apply a stress at high temperature to produce only elastic strain but that will be sufficiently high to stress-induce the favoured martensite variants by cooling. The ductilities are sufficiently high to sustain the high strain that may be produced by these stress-induced martensites during cooling and sufficient training should lead to induce the desired two way shape memory effect.

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